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itaconic anhydride, citraconic anhydride, ethyl acrylate, methyl methacrylate, ethyl maleate, 2-ethylhexyl acrylate, acrylamide, methacrylamide, coconut fatty acid amide and maleimide. In addition, as the adhesive resin, there can be used ethylene-acrylate copolymers, ionomers (such as Surlyn ® manufactured by Du Pont), polyalkylene oxide-polyester block copolymers, carboxylmethyl cellulose derivatives, and blends of these polymers with polyolefins.

In order to draw a parison or sheet having a multilayer structure under the above-mentioned conditions, the melting or softening point of the adhesive resin is limited.

More specifically, the melting or softening point (T_C, °C.) of the adhesive resin (C) should be lower than the melting or softening point (T_O, °C.) of the orienting thermoplastic resin (B), and in view of the interlaminar peel strength and moldability of a multi-layer parison or sheet to be drawn, it is preferred that the requirement represented by the following formula:

$$90° C. \geq T_O - T_C \geq 1° C. \qquad (7)$$

wherein T_O stands for the melting or softening point (°C.) of the orienting thermoplastic resin (B) and T_C stands for the melting or softening point (°C.) of the adhesive resin (C), be satisfied.

Multi-Layer Structure

The layer structure of the multi-layer container is preferably decided according to the use and physical properties of the container. For example, when the content is a non-aqueous content, a layer of a chemically inactive resin such as a polyolefin need not be used as the innermost layer, but when the content is a food or drink, it is preferred to use a polyolefin considered to be safest from the sanitary viewpoint as the innermost layer. Layer structures including an oxygen-barrier thermoplastic resin layer (designated as "A") and an orienting thermoplastic resin layer (designated as "B" or "B'") optionally with an adhesive resin layer (designated as "C"), which are preferably used in this invention, are as follows:

(i)	Two-Layer Structure:	
	B/A	(i)
(ii)	Three-Layer Structure:	
	B/C/A	(ii-1)
	B/A/B	(ii-2)
	B/A/B'	(ii-3)
(iii)	Four-Layer Structure:	
	B/B'/C/A	(iii-1)
	B/C/A/C	(iii-2)
	B/C/A/B'	(iii-3)
(iv)	Five-Layer Structure:	
	B/C/A/C/B	(iv-1)
	B/C/A/C/B'	(iv-2)
	(B + A + C)/C/A/C/(B + A + C)	(iv-3)
(v)	Six-Layer Structure:	
	B/B'/C/A/C/B	(v-1)
	B/(B + A + C)/C/A/C/B	(v-2)
(vi)	Seven-Layer Structure:	
	B/(B + A + C)/C/A/C/(B + A + C)/B	(vi-1)
	B/B'/C/A/C/B'/B	(vi-2)

Among these multi-layer structures, five-layer structures (iv-1), (iv-2) and (iv-3) and seven-layer structure (vi-1) are especially preferred.

It is preferred that in the above-mentioned multi-layer structure, 0.2 to 50%, especially 2 to 20%, of the

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total thickness of the final container be occupied by the oxygen-barrier resin layer (A).

Further, it is preferred that the respective resin layers be present in the multi-layer structure at the following thickness ratios:

B:A=from 1:1 to 500:1

and

B:C=from 1:1 to 500:1

Container

In the intended multi-layer draw-molded container or multi-layer solid phase pressure-formed container of the present invention, all the layers constituting the container should not necessarily be draw-molded or solid phase pressure-formed. In this invention, a resin layer in which a relatively excellent transparency cannot be obtained according to the conventional melt-molding method is draw-molded or solid phase pressure-formed. In this invention, it is important to select layer-constituting resins so that at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the final container is at least 0.05.

The two-dimensional orientation coefficients referred to in the instant specification and appended claims can be determined according to the method described in "Polymers, vol. 15, No. 175, page 868" written by Yasunori Nishijima and published by Japanese Association of Polymers in 1966, in which by utilizing optically anisotropic characteristics of a fluorescent molecule, the degree and mode of molecular orientation of a polymer, i.e., a thermoplastic resin, caused by solid deformation or by flowing in the solution or melt state are qualitatively and quantitatively determined. When the two-dimensional orientation in the wall face of the container of this invention is considered in the light of teachings of the above literature reference, the two-dimensional orientation degrees can be quantitatively represented as follows:

$$I_{//}(\omega) = K + (l\cos^4\omega + m\sin^4\omega + (1/3)n) \qquad (8)$$

wherein $I_{//}(\omega)$ stands for the intensity of the polarized component of the fluorescence emitted from a thermoplastic resin as the sample, // indicates that the vibration direction of incident polarized light is in parallel to the direction of measured polarized light, ω stands for the rotation angle of the sample with respect to the vibration direction of said polarized light, K designates a maximum excitation probability when the molecular axis of the sample is in parallel to the vibration direction of excited fluorescent light, ϕ stands for the molecular fluorescent contraction, l designates the ratio of orientation of the molecule in one optional direction in the wall face of the container, m designates the ratio of orientation in a direction rectangular to the orientation direction of l, n stands for the ratio of non-orientation in the wall face, and the sum of l, m and n is 1 (l+m+n=1). When the adhesive resin (C) is interposed between the oxygen-barrier resin layer (A) and the orienting resin layer (B), it is preferred that the adhesive resin layer (C) be substantially non-oriented.

In accordance with another preferred embodiment of this invention, there is provided a multi-layer container wherein the oxygen-barrier resin and the orienting resin

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are selected so that the requirement represented by the following formula:

$$\|T_B - T_O\| \le 10^\circ C. \tag{7}$$

wherein T_B and T_O are as defined above, is satisfied, at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the orienting thermoplastic resin in a smallest-thickness portion of the container is at least 0.1, each resin layer has a haze (Hz) lower than 10%, and wherein the bonding strength between every two adjacent layer is at least 20 g/cm.

In order to obtain a container having much preferred transparency and rigidity, it is important that the difference Δt should be not larger than 10° C. and at least one of two-dimensional orientation coefficients (l and m) should be at least 0.1. When at least one of the two-dimensional orientation coefficients of the orienting resin layer is at least 0.1, namely when the orienting resin layer is drawn at a relatively high draw ratio, there is observed a tendency that the bonding strength between adjacent layers is reduced, as pointed out hereinbefore. However, we found that if each layer constituting the container has a haze (Hz) lower than 10%, namely if each layer is excellent in the transparency, the peeling is not visually noted under shaking or falling between two adjacent layers, and that this effect can be prominently attained if the interlaminar bonding strength between every two adjacent layers is at least 20 g/cm.

The molded container of this invention has a unit volume (the volume per unit weight, g, of the resin) of 0.01 to 5 dl/g, especially 0.05 to 2 dl/g, though the unit volume is changed to some extent depending on the intended use of the container. The wall thickness of the container of this invention is adjusted in a range of from 0.02 to 1 mm, especially from 0.08 to 0.8 mm. When the unit volume and wall thickness are appropriately chosen within these ranges, a preferred combination of high interlaminar peel strength, high gas-barrier property, high rigidity and high transparency can be attained.

Preparation Process

The container of this invention can be prepared according to a process comprising forming a parison or sheet having the above-mentioned multi-layer structure by co-melt-extrusion, and molding the parison or sheet into a container at a molding temperature (Tm) satisfying the requirement represented by the following formula:

$$|T_m - T_B| \le 30^\circ C. \tag{8}$$

wherein T_B is as defined above and Tm stands for the molding temperature ($^\circ$C.), and under such conditions that orientation of the orienting thermoplastic resin is caused at least in a smallest-thickness portion of the container.

A parison or sheet having the above-mentioned multi-layer structure can be formed by known molding means. For example, a multi-layer parison can be prepared by concurrent extrusion or injection molding of the above-mentioned resins in a layer structure as mentioned hereinbefore. Further, a multi-layer sheet can be prepared by extruding the above-mentioned resins in a multi-layer structure as mentioned hereinbefore according to known means and molding the extrudate into a sheet according to the known T-die molding method.

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The so obtained laminate sheet may be subjected to a post treatment such as rolling.

The importance that the temperature (Tm) for molding the multi-layer parison or sheet under drawing should be in the range satisfying the requirement represented by the formula (8) will be apparent from the illustration given hereinbefore with respect to the resin components.

When the adhesive resin layer (C) is interposed between the oxygen-barrier thermoplastic resin layer (A) and the orienting resin layer (B), it also is important that the multi-layer parison or sheet should be monoaxially or biaxially draw-molded at a temperature (Tm) higher than the melting or softening point (T_C) of the adhesive resin (C) but lower than the melting or softening point (T_O) of the orienting thermoplastic resin (B).

When monoaxial or biaxial draw-molding is carried out at a temperature (Tm) satisfying the requirement represented by the following formula:

$$T_O > T_m \ge T_C \tag{9}$$

according to a preferred embodiment of this invention, drawing is effected while the orienting thermoplastic resin (B) is in the non-softened state and the adhesive resin (C) is in the molten or softened state, and while effective orientation can be given to the orienting thermoplastic resin, the interlaminar peel strength between the orienting thermoplastic resin layer (B) and the oxygen-barrier thermoplastic resin layer (A) can be remarkably enhanced. When draw-molding is carried out at a temperature lower than the melting or softening point of the adhesive resin (C), as shown in Example 7 given hereinafter (see comparative bottle BB), in the resulting draw-molded bottle, delamination is readily caused between the oxygen-barrier resin layer (A) and the orienting resin layer (B) under falling shock or the like. On the other hand, as shown in Example 7 given hereinafter, when draw-molding is carried out at a temperature higher than the melting or softening point of the orienting resin (B), a heated parison (parison will be often referred to as "pipe" hereinafter) is poor in the form-retaining property and it is readily deformed, and it sometime become impossible to perform draw-molding. If draw-molding be possible, the resulting bottle is insufficient in such properties as transparency and smoothness.

In contrast, when the multi-layer parison or sheet is draw-molded at a temperature (Tm) higher than the melting or softening point of the adhesive resin but lower than the melting or softening point of the orienting resin according to this invention, as shown in Examples given hereinafter, a draw-molded container excellent in such properties as rigidity, mechanical strength, transparency and smoothness can be obtained with good moldability and processability. Moreover, the interlaminar peel strength between the oxygen-barrier resin layer (A) and the orienting resin layer (B) can be enhanced to a level exceeding 135 g/cm of the width, and in the resulting container, delamination is not substantially caused under falling shock.

The reason why the interlaminar strength of the container can be prominently improved by conducting draw-molding under the above-mentioned temperature condition according to the present embodiment of this invention has not been completely elucidated, but it is construed that main causes are as follows.

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The adhesive resin (C) in the molten or softened state at the draw-molding step has an action of moderating stress or strain generated on the interface between the two resin layers at the draw-molding step, and the interposed adhesive resin (C) present in the molten or softened state promotes drawing of the orienting resin layer (B) or the oxygen-barrier resin layer (A).

Under the above-mentioned draw-molding temperature condition of this embodiment the oxygen-barrier resin layer (A) may be in the molten or softened state or in the non-molten or non-solidified state. For example, when the oxygen-barrier resin (A) is an ethylenevinyl alcohol copolymer, it is preferred that monoaxial or biaxial drawing be carried out while the copolymer is in the molten or softened state. In case of monoaxial drawing, the copolymer may be kept in the non-molten or semi-molten state. On the other hand, when the oxygen-barrier resin (A) is a polyamide resin, in general, there is not such condition.

A hot air circulating passage, an infrared heater, an induction heater, a microwave irradiator, a heater for contact with a heating medium such as steam or heated oil or a combination of these heating means can be used for maintaining the multi-layer parison or sheet at the above-mentioned draw-molding temperature (Tm). Of course, it is possible to perform draw-molding when the temperature of an as-molded parison or sheet having the above-mentioned molded structure is lowered to the above-mentioned draw-molding temperature.

In this invention, in view of such properties as rigidity, mechanical strength and transparency of the resulting container, it is preferred that the multi-layer parison or sheet be drawn to such an extent that at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the orienting resin in a smallest-thickness portion of the container is at least 0.05.

For attaining this feature, in general, it is preferred that the draw ratio of the multi-layer parison or sheet be 1.1 to 20, especially 1.5 to 5. The drawing speed at the step of forming the multi-layer parison or sheet into a container differs depending on the kind of the resin, and the drawing speed is appropriately decided within a range causing the above-mentioned drawing effect. It is especially preferred that the drawing speed be in a range of from 10%/mm to 6,000,000%/mm.

In this invention, draw-molding of the multi-layer parison or sheet into a container can be performed under the same conditions as known molding conditions except that the molding temperature (Tm) is maintained within the above-mentioned range and drawing is carried out to such an extent that at least one of two-dimensional orientation coefficients (l and m) is at least 0.05, especially at least 0.1.

For example, formation of a bottle from the multi-layer parison can be accomplished by drawing of the parison in the axial direction by holding means or a mandrel and drawing of the parison in the lateral direction by blow-in of a fluid. Steps of drawing the parison in the axial direction and in the lateral direction may be conducted concurrently or in sequence.

Formation of a container such as a cup from the multi-layer sheet can be accomplished by plug-assist forming (vacuum molding), air-pressure forming, sheet blow molding, draw forming, draw-ironing molding, compression molding, forward extrusion, backward extrusion, forward-backward extrusion and explosion forming. In the instant specification, these forming methods are collectively called "draw forming method".

When draw-molding is carried out under the above-mentioned conditions according to this invention, a container excellent in transparency, rigidity and gas-barrier property and having especially high interlaminar peel strength can be obtained. Further, by virtue of the drawing effect, it is made possible to reduce the wall thickness of the container, decrease the weight of the container and reduce amounts used of resins drastically.

Uses

The container of this invention has a desirable combination of gas-barrier property, rigidity, transparency and interlaminar peel strength, and they can be valuably applied to various uses.

Because of these advantages, the container of the present invention is very useful for preserving, without substantial deterioration or quantity loss, various liquid and pasty foods and drinks, for example, bubbling alcoholic drinks such as beer, other alcoholic drinks such as Japanese sake, whisky, distilled spirits, wines, gin fizz and other cocktails, carbonated drinks such as cola, cider and plain soda, fruit drinks such as straight fruit juices, e.g., lemon juice, orange juice, plum juice, grape juice and strawberry juice and processed fruit juices, e.g., Nectar ®, vegetable juices such as tomato juice, synthetic drinks and vitamin-incorporated drinks formed by blending a saccharide such as sugar or fructose, citric acid, a colorant and a perfume optionally with vitamins, lactic acid beverages, stews, e.g., pre-cooked curry, pre-cooked hash, borsch and beef stew, gravy, e.g., meat sauce, boiled vegetables, fishes and meats, e.g., vinegared pork, sukiyaki, Chinese food paste of beef and vegetables, Chinese hotchpotch, boiled spinach, boiled mushroom, boiled asparagus, boiled beans, boiled corn and cream-boiled tuna, soups, e.g., consome soup, potage soup, miso soup, pork-incorporated miso soup and vegetable soup cooked with oil, rice foods, e.g., boiled rice, rice boiled with red beans, toasted boiled rice, frizzled boiled rice, pilaff and rice-gruel, noodles, e.g., spaghetti, buck-wheat vermicelli, wheat vermicelli, Chinese noodle and Italian noodle, compound condiments, e.g., those for toasted boiled rice or Chinese noodle soup, luxury foods, e.g., tasted boiled red beans, thick and thick bean-meal soups with sugar, sugared and boiled beans with rice cake or fruits and jelly, boiled beans with treacle poured on, custard pudding, jelly cakes and soft adzuki-bean jelly, processed fish and meat products, e.g., meat dumpling, hamburger, corn beaf, ham, sausage, roast fish, smoked fish, bacon and boiled fish paste, fruit products, e.g., processed orange, peach, pine-apple, cherry and apple, condiments such as soy, sauce, vinegar, sweet sake, dressing, mayonnaise, ketchup, soybean paste, lard and edible oil, and foods such as bean curd, jam, butter and margarine; liquid medicines, liquid agricultural chemicals, liquid cosmetics and detergents; ketones such as acetone and methylethyl ketone; aliphatic hydrocarbons such as n-hexane and n-heptane; alicyclic hydrocarbons such as cyclohexane; aromatic hydrocarbons such as benzene, toluene and xylene; chlorine-containing carbon tetrachloride, tetrachloroethane and tetrachloroethylene; liquid fuels and oils such as gasoline, kerosine; petroleum bendine, fuel oil, thinner, grease, silicone oil, light oil and machine oil; and liquefied Freon (the trademark of a product manufactured by Du Pont).

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This invention will now be described by reference to the following Examples that by no means limit the scope of the invention.

EXAMPLE 1

Parisons having both the ends opened and having an inner diameter of 10 mm, a length of 185 mm and a thickness of 7.5 mm and parisons having both the ends opened and having an inner diameter of 15 mm, a length of 100 mm and a thickness of 4.5 mm were prepared from the following 24 combinations of innermost and outermost layers, intermediate layers and adhesive layers by using an extruder for forming innermost and outermost layers, which included a full-flighted screw having a diameter of 65 mm and an effective length of 1430 mm and was provided with a melt channel divided into two flow passages, an extruder for forming adhesive layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm and was provided with a melt channel divided into two flow passages, an extruder for forming intermediate layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, a 5-ply die, a pipe former and a pipe cutter.

Resins used for formation of intermediate layers are as follows:

EV1:

Ethylene-vinyl alcohol copolymer having an ethylene content of 45 mole %, a vinyl alcohol content of 55 mole %, a melting point of 154° C. as measured according to the differential thermal analysis method (hereinafter referred to as "DTA method") in which the temperature-elevating rate was 10° C./mm, and an oxygen permeability (PO_2) of 0.23×10^{-12} cc-cm/cm²-sec-cmHg as measured at a temperature of 37° C. and a relative humidity of 0%.

EV2:

Ethylene-vinyl alcohol copolymer having an ethylene content of 30 mole %, a vinyl alcohol content of 70 mole %, a melting point of 181° C. as measured according to the above-mentioned DTA method and an oxygen permeability of 0.07×10^{-12} cc-cm/cm²-sec-cmHg as measured under the above-mentioned conditions.

EV3:

Ethylene-vinyl alcohol copolymer having an ethylene content of 19 mole %, a vinyl alcohol content of 81 mole %, a melting point of 197° C. as measured according to the above-mentioned DTA method and an oxygen permeability of 0.059×10^{-12} cc-cm/cm²-sec-cmHg as measured under the above-mentioned conditions.

EV4:

Ethylene-vinyl alcohol copolymer having an ethylene content of 66 mole %, a vinyl alcohol content of 34 mole %, a melting point of 120° C. as measured according to the above-mentioned DTA method and an oxygen permeability of 5.4×10^{-12} cc-cm/cm²-sec-cmHg as measured under the above-mentioned conditions.

Resins used for formation of innermost and outermost layers are as follows:

PP1:

Isotactic polypropylene having a density of 0.909 g/cc and a melting point of 159° C. as measured according to the above-mentioned DTA method.

PP2:

Ethylene-propylene random copolymer having a density of 0.90 g/cc, a melting point of 154° C. as measured according to the above-mentioned DTA method and an ethylene content of 10 mole %.

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Resins used for formation of adhesive layers are as follows:

AH1:

Unsaturated carboxylic acid-modified polypropylene having a density of 0.90 g/cc and a melting point of 159° C. as measured according to the above-mentioned DTA method.

AH2:

Unsaturated carboxylic acid-modified polypropylene having a density of 0.90 g/cc and a melting point of 154° C. as measured according to the above-mentioned DTA method.

AH3:

Resin blend having a density of 0.90 g/cc and being composed of unsaturated carboxylic acid-modified polyethylene having a melting point of 105° C. as measured according to the above-mentioned DTA method and an unsaturated carboxylic acid-modified polypropylene having a melting point of 155° C. as measured according to the above-mentioned DTA method.

These pipes (parisons) were heated for about 30 minutes in a hot air-circulated oven maintained precisely at an atmosphere temperature of 155° C. Then, pipes having an inner diameter of 10 mm, a length of 185 mm and a thickness of 4.5 mm were formed into bottles having a thickness of 0.6 mm, an inner capacity of 300 cc and a weight of 22 to 24 g/bottle according to the sequent biaxial draw-blowing method at a draw ratio of 3 in the longitudinal direction (the bottle height direction) and at a draw ratio of 3.5 in the lateral direction (the bottle circumference direction). Bottles having the same dimensions as described above were prepared from pipes having an inner diameter of 15 mm, a length of 100 mm and a thickness of 4.5 mm according to the same sequent biaxial draw-blowing method at a draw ratio of 1.5 in the longitudinal direction and at a draw ratio of 1.5 in the lateral direction.

For comparison, cylindrical multi-layer bottles having the same dimensions as described above were prepared from some of 24 combinations according to the known direct blow-molding method (blow-molding of molten parisons) in which multi-layer parisons as-extruded from the 5-ply die and in the molten state were immediately blow-molded.

In each case, the molding was carried out carefully so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:1:3 as possible.

With respect to each of the so prepared 58 kinds of bottles, the oxygen transmission rate (QO_2), the haze (Hz) and the orientation coefficients (1, m and n) of the innermost and outermost layers were determined according to the method disclosed in Japanese Patent Application Laid-Open Specification No. 49379/75, the measuring method of JIS K-6714 and the above-mentioned fluorescence method, respectively. Further, with respect to each kind of bottles, 10 sample bottles were chosen and 340 g of an aqueous solution of table salt was filled in each bottle. Then, the filled bottles were allowed to stand in an atmosphere maintained at −1° C. over 3 days and nights, and immediately, they were let to fall on a concrete floor from a height of 1.2 m in an atmosphere maintained at 20° C. so that bottle bottoms were caused to hit on the concrete floor. Then, the falling strength represented by the following formula:

$$F_g = 100 \times [10 - F_1]/10$$

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wherein F_1 stands for the number of bottles broken at the first falling test and F_B denotes the falling strength, was determined. Further, occurrence of delamination was visually examined by a panel of 5 men (the occurrence of delamination was evaluated based on an average value of the number N of bottles where delamination took at the first falling test). From each bottle, specimens having a width of 10 mm and a length of 50 mm were cut off in both the vertical direction and circumferential direction of the bottle wall, and the peel strength (AT) was measured at a peeling rate of 100 mm/min in an atmosphere maintained at a temperature of 20° C. and a relative humidity of 60%. Results of these tests are shown in Table 3.

In Table 3, symbols of bottles are expressed by numbers of four figures. The thousands digit indicates the material of the intermediate layer. For example, "1", "2", "3" and "4" indicate EV1, EV2, EV3 and EV4, respectively. Similarly, the hundreds digit indicates the material of the adhesive layer and the tens digit indicates the material of the outermost and innermost layers, and the expression manner is the same as in case of the intermediate layer. The units digits indicate kinds of bottles. More specifically, "1", "2" and "3" represent a draw-blow molded bottle drawn at a draw ratio of 1.5 in the longitudinal direction and at a draw ratio of 1.5 in the lateral direction, a draw-blow molded bottle drawn

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at a draw ratio of 3.5 in the lateral direction and at a draw ratio of 3 in the longitudinal direction, and a comparative bottle formed by the above-mentioned direct blow-molding method, respectively. For example, symbol 2122 indicates a biaxially drawn blow-molded bottle comprising an intermediate layer of EV2, an adhesive layer of AH1 and innermost and outermost layers of PP1, in which the draw ratio in the lateral direction is 3.5 and the draw ratio in the longitudinal direction is 3.

From the results shown in Table 3, it will readily be understood that biaxially drawn blow-molded bottles are apparently excellent over directly blow-molded bottles with respect to the oxygen barrier property and transparency, and that although the directly blow-molded bottles are excellent over biaxially drawn blow-molded bottles with respect to the adhesion strength, the latter bottles are excellent over the former bottles with respect to the interlaminar peel strength determined by the visual test, namely the practical peel strength. It will also be understood that if the intermediate layer excellent in the barrier property to gases such as oxygen is selected so that the above-mentioned requirements of this invention are satisfied, the oxygen-barrier property, transparency and interlaminar peel strength can be remarkably improved in the resulting container.

Table 3

Symbol of Bottle	QO₂ cc/cm². day . atm	Hz[%]			Orientation Co-efficients (innermost and outermost layers)		
		Intermediate Layer	Innermost and Outermost Layers plus Adhesive Layer	Bottle	l	m	n
1111	7.3	<1	13	14	0.11	0.12	0.77
1112	6.0	<1	7	8	0.23	0.32	0.45
1113	8.0	<2	30	33	0.02	0.03	0.95
1121	7.2	<1	12	13	0.07	0.09	0.84
1122	6.1	<1	6	6	0.15	0.19	0.66
1123	9.0	<2	23	24	0.03	0.02	0.95
1211	7.2	<1	12	13	0.09	0.10	0.81
1212	6.2	<1	7	7	0.22	0.31	0.47
1213	8.1	<2	31	33	0.01	0.02	0.97
1221	7.1	<1	13	14	0.09	0.11	0.80
1222	6.1	<1	6	7	0.14	0.18	0.68
1223	8.2	<2	22	23	0.03	0.04	0.93
1311	7.2	<1	14	15	0.15	0.14	0.71
1312	6.4	<1	7	8	0.21	0.25	0.54
1313	8.1	<2	31	32	0.02	0.03	0.95
1321	7.3	<1	12	12	0.08	0.08	0.84
1322	6.4	<1	6	6	0.13	0.18	0.69
1323	8.0	<2	24	25	0.01	0.04	0.95
2111	2.4	<1	13	15	0.10	0.11	0.79
2112	2.1	<1	7	9	0.25	0.32	0.43

Symbol of Bottle	Falling Test		Peel Strength (g/cm of width)	
	F_B(%)	(number of bottles)	Vertical direction of bottle	Circumferential direction of bottle
1111	90	1	126	132
1112	100	0	32	40
1113	40	2	221	230
1121	100	0	151	152
1122	100	0	29	38
1123	70	1	230	241
1211	90	0	131	140
1212	100	0	22	31
1213	40	1	218	221
1221	100	1	142	153
1222	100	0	63	72
1223	70	2	292	291
1311	80	0	141	156
1312	100	0	69	83
1313	40	1	289	293
1321	100	0	152	163
1322	100	0	76	84
1323	90	0	288	296

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Table 3-continued

2111	90	0	143	161
2112	100	0	58	73

Symbol of Bottle	QO_2 cc/m² . day . atm.	Intermediate Layer	Innermost and Outermost Layers plus Adhesive Layer	Bottle	Orientation Co-efficients (innermost and outermost layers) l	m	n
			Hz(%)				
2113	2.8	<1	30	32	0.02	0.03	0.95
2121	2.3	<1	12	13	0.08	0.09	0.83
2122	2.2	<1	6	7	0.14	0.19	0.67
2123	2.9	<1	23	25	0.02	0.03	0.95
2211	2.4	<1	11	12	0.09	0.09	0.82
2212	2.2	<1	7	7	0.21	0.28	0.51
2213	3.1	<1	30	32	0.02	0.03	0.95
2221	2.3	<1	12	13	0.08	0.08	0.84
2222	2.1	<1	6	7	0.15	0.20	0.65
2223	2.9	<1	22	23	0.01	0.04	0.95
2311	2.2	<1	14	15	0.10	0.08	0.82
2312	2.0	<1	7	8	0.28	0.32	0.40
2321	2.9	<1	12	14	0.09	0.08	0.83
2322	2.1	<1	6	7	0.14	0.20	0.66
3111	2.0	<1	13	15	0.11	0.09	0.80
3112	35.0	<1	7	7	0.24	0.25	0.47
3121	2.1	<1	12	13	0.08	0.09	0.83
3122	1.9	<1	6	7	0.14	0.20	0.66
3211	2.0	<1	11	13	0.10	0.09	0.81
3212	21.0	<1	7	8	0.24	0.28	0.48

Symbol of Bottle	Falling Test F_B (%)	(number of bottles)	Peel Strength (g/cm of width) Vertical direction of bottle	Circumferential direction of bottle
2113	40	1	291	301
2121	100	0	150	158
2122	100	0	59	76
2123	70	2	293	294
2211	90	0	146	153
2212	100	0	53	72
2213	30	1	289	293
2221	100	0	151	161
2222	100	0	59	78
2223	60	1	291	293
2311	100	0	145	146
2312	100	0	52	63
2321	100	0	138	151
2322	100	0	72	71
3111	90	1	109	113
3112	100	2	15	19
3121	100	1	111	114
3122	100	2	20	19
3211	80	1	99	103
3212	100	1	17	21

Symbol of Bottle	QO_2 cc/m² . day . atm	Intermediate Layer	Innermost and Outermost Layers plus Adhesive Layer	Bottle	Orientation Co-efficients (innermost and outermost layers) l	m	n
			Hz(%)				
3221	2.0	<1	12	14	0.07	0.08	0.85
3222	2.2	<1	6	7	0.15	0.19	0.66
3311	1.9	<1	14	15	0.12	0.11	0.77
3312	24.0	<1	7	7	0.21	0.27	0.52
3321	2.1	<1	12	15	0.09	0.09	0.82
3322	53.0	<5	6	7	0.14	0.018	0.68
4111	95.0	<5	15	17	0.10	0.11	0.79
4112	78.2	<5	11	12	0.21	0.27	0.52
4121	91.0	<5	13	18	0.08	0.09	0.83
4122	76.0	<5	10	12	0.14	0.16	0.70
4211	83.0	<5	14	15	0.12	0.11	0.77
4212	80.0	<5	11	13	0.23	0.31	0.46
4221	93.0	<5	14	16	0.09	0.08	0.83
4222	73.2	<5	11	12	0.15	0.23	0.62
4311	86.5	<5	15	17	0.13	0.11	0.76
4312	72.4	<5	12	14	0.22	0.34	0.44
4321	91.3	<5	15	16	0.08	0.09	0.83
4322	70.7	<5	10	12	0.14	0.22	0.64

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Table 3-continued

Symbol of Bottle	Falling Test		Peel Strength (g/cm of width)	
	F_B (%)	(number of bottles)	Vertical direction of bottle	Circumferential direction of bottle
3221	100	1	115	116
3222	100	2	21	23
3311	80	1	103	106
3312	90	1	19	21
3321	100	2	139	141
3322	100	2	21	23
4111	90	2	117	121
4112	100	1	31	29
4121	100	2	117	118
4122	100	2	29	33
4211	90	1	119	123
4212	100	1	31	42
4221	100	0	120	131
4222	100	1	41	52
4311	80	1	125	128
4312	100	0	51	62
4321	90	0	131	130
4322	100	1	61	99

EXAMPLE 2

Symmetric 5-layer sheets having a thickness of 0.8 mm and a width of 450 mm were formed by using an extruder for forming innermost and outermost layers, which included a full-flighted screw having a diameter of 65 mm and an effective length of 1430 mm, an extruder for forming adhesive layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, an extruder for forming intermediate layers, which included a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, a T-die equipped with a multi-channel adaptor and having a lip width of 0.6 mm and a lip length of 500 mm, and a sheet-forming machine. The ethylene-vinyl alcohol copolymers EV1, EV2, EV3 and EV4 described in Example 1 were used as the intermediate layer-constituting material. An ethylene-propylene copolymer having a density of 0.9 g/cc, a melting point of 156° C. as measured according to the DTA method, a melt index of 1.6 dg/min as measured according to the method of JIS K-6758 and an ethylene content of 10 mole % was used as the material of the innermost and outermost layers. An unsaturated carboxylic acid-modified ethylene-propylene copolymer having a density of 0.90 g/cc, a melting point of 154° C. as measured according to the DTA method and a melt index of 2.0 dg/min as measured according to the above-mentioned method was used as the adhesive layer-constituting material. The sheet forming operation was carried out by adjusting the amounts of resins extruded from the three extruders so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:1:3 as possible. The so formed 4 kinds of sheets were heated for about 15 minutes in a hot air-circulated oven having an atmosphere maintained precisely at 155° C. and they were formed into cups having a diameter of 85 mm, a height of 50 mm, an inner capacity of 300 cc and a unit weight of 9 to 10 g/cup according to the plug assist vacuum forming method disclosed in the specification of co-pending U.S. Application Ser. No. 750,376.

For comparison, cylindrical cups having the same dimensions as described above were formed from the above-mentioned 4 kinds of sheets according to the conventional sheet-blowing method, in which the sheets as-extruded from the T-die and in the molten state were blow-molded.

Cups formed according to the plug assist vacuum forming method (solid phase forming method) using EV1 as the intermediate layer are designated as "SP1", and cups formed by the molten sheet blow-molding method using EV1 are designated as "SB1". Similarly, cups formed by using EV2, EV3 and EV4 according to the plug assist vacuum forming method are designated as "SP2", "SP3" and "SP4", respectively, and cups formed by using EV2, EV3 and EV4 according to the molten sheet blow-molding method are designated as "SB2", "SB3" and "SB4", respectively.

With respect to each of the foregoing 8 kinds of cups, the oxygen transmission rate (QO_2), the haze (Hz) and the orientation coefficients (l, m and n) were determined according to the methods described in Example 1. Further, 10 sample cups were chosen from each kind of cups, and 340 g of an aqueous solution of table salt was filled in each cup. The filled cups were allowed to stand in an atmosphere maintained at −1° C. over 3 nights and days, and immediately, the cups were subjected to the free vibration test under conditions of a vibration frequency of 400 cpm, a vibration amplitude of 20 mm and an acceleration of 1.8 G for 30 minutes by using a Matsudaira type vibration tester and the number (N) of broken cups were counted. Further, occurrence of delamination was visually tested by a panel of 5 men (the occurrence of delamination was evaluated based on an average number (ADN) of cups where delamination took place). The thickness unevenness of the intermediate layer in molded cups was examined in both the vertical and circumferential direction of the cup and standard deviations δL and δH were determined. Results of these tests are shown in Table 4.

As will be apparent from the results shown in Table 4, the solid phase pressure-formed cups are excellent over directly melt-molded cups with respect to the oxygen-barrier property and transparency. It will also be understood that if the intermediate layer is selected so that the requirements of this invention are satisfied, the resulting cups (samples SP1 and SP2) are much excellent in the interlaminar peel strength and the thickness uniformity of the intermediate layer.

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Table 4

Symbol of Cup	QO2 cc/m² . day . atm	Hf[%]			Orientation Coefficients (innermost and outermost layers)		
		Intermediate Layer	Innermost and Outermost Layers plus Adhesive Layer	Cup	l	m	n
SP1	8.3	<1	7	8	0.31	0.13	0.56
SP2	3.1	<1	6	7	0.41	0.09	0.50
SP3	3.0	<1	6	7	0.29	0.15	0.56
SP4	93.2	<1	16	18	0.32	0.15	0.53
SB1	13.2	<2	23	24	0.03	0.01	0.96
SB2	10.1	<2	22	22	0.04	0.02	0.94
SB3	9.6	<2	21	22	0.02	0.01	0.97
SB4	14.7	<2	23	24	0.03	0.01	0.96

Symbol of Cup	Results of Vibration Test		Thickness Unevenness of Intermediate Layer	
	N	ADN	δL	δH
SP1	0	0	0.20	-0.09
SP2	0	0	0.15	0.09
SP3	0	2	0.23	0.10
SP4	0	1	0.62	0.31
SB1	0	1	0.21	0.13
SB2	1	1	0.22	0.12
SB3	0	2	0.20	0.15
SB4	1	3	0.21	0.11

EXAMPLE 3

By using the same molding equipment as used in Example 1, symmetric five-layer parisons composed of three kinds of resins were prepared, and bottles having a symmetric 5-layer structure were formed from these parisons according to the sequent biaxial draw-blow forming method in which the drawing operation was carried out at 159° C. at a draw ratio of 3 in the longitudinal direction and at a draw ratio of 3.5 in the lateral direction. An ω-aminocaproic acid polymer (N1) having a melting point of 223° C. as measured according to the DTA method, a relative viscosity of 1.9 as measured with respect to a solution of 1 g of the polymer in 100 cc of 98% concentrated sulfuric acid and an oxygen permeability of 4.0×10^{-13} cc-cm/cm²-sec-cmHg as measured at a temperature of 37° C. and a relative humidity of 0% and a caprolactam/hexamethylene diammonium adipate copolymer (N2) having a melting point of 163° C. as measured according to the DTA method, a relative viscosity of 3.4 as measured in the same manner as described above, an oxygen permeability of 3.5×10^{-12} cc-cm/c-m²-sec-cmHg as measured in the same manner as described above and a caprolactam concentration of 81 mole % were used as the intermediate layer-constituting material. An unsaturated carboxylic acid-modified polypropylene having a density of 0.90 g/cc and a melting point of 156° C. as measured according to the DTA method was used as the material of the adhesive layer adjacent to the intermediate layer. An isotactic polypropylene having a density of 0.909 g/cc and a melting point of 160° C. as measured according to the DTA method was used as the material constituting the innermost and outermost layers.

For comparison, with respect to each of the foregoing two combinations of resins, in the same manner as described in Example 1, bottles were formed from multi-layer parisons extruded from the 5-ply die and still in the molten state according to the direct blow molding method.

Configurations of the so formed 4 kinds of bottles were the same as those described in Example 1. The amounts of resins extruded from the three extruders were adjusted so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:2:1 as possible.

With respect to each of these 4 kinds of bottles, the oxygen transmission rate (QO2), haze (Hz), orientation coefficients, falling strength (F$_B$) and interlaminar peel strength were determined according to the same methods as described in Example 1, and the number (N) of broken bottles and occurrence of delamination at the vibration test and the standard deviations δL and δH indicating the thickness unevenness of the intermediate layer were determined according to the same methods as described in Example 2. Results of these tests are shown in Table 5. In Table 5, bottle symbols indicate the following bottles:

BO1:
Biaxially drawn blow-formed bottles containing N1 as the intermediate layer-constituting material.

BO2:
Biaxially drawn blow-formed bottles containing N2 as the intermediate layer-constituting material.

DO1:
Directly blow-molded bottles (formed by blow molding of molten parisons) containing N1 as the intermediate layer-constituting material.

DO2:
Directly blow-molded bottles containing N2 as the intermediate layer-constituting material.

From the results shown in Table 5, it will readily be understood that BO2 bottles formed by selecting the intermediate layer so that the requirements of the present Invention are satisfied are much excellent in the oxygen-barrier property, falling strength, strength and delamination resistance at the vibration test and thickness uniformity of the intermediate layer.

Table 5

Hf[%]

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Table 5-continued

Symbol of Bottle	QO2 cc/m². day . atm	Interme-diate Layer	Innermost and Outermost Layers plus Adhesive Layer	Bottle	Orientation Coefficients (innermost and outermost layers)		
					I	m	n
BO1	56.2	<2	7	8	0.23	0.31	0.46
BO2	19.1	<2	6	7	0.22	0.30	0.48
DO1	41.5	<5	31	33	0.02	0.01	0.97
DO2	36.9	<5	32	34	0.03	0.02	0.95

Symbol of Bottle	Falling Test Results		Vibration Test Results		Thickness Unevenness of Intermediate Layer	
	FB (%)	N (number of broken bottles)	N	ADN	δL	δH
BO1	100	3	0	1	0.35	0.12
BO2	100	8	0	0	0.15	0.09
DO1	40	0	0	0	0.21	0.10
DO2	50	1	1	1	0.20	0.11

EXAMPLE 4

Sheets having a thickness of 0.5 mm and a width of about 400 mm and having a symmetric 5-layer structure were prepared by using a known extruding and sheet-forming machine.

The same ω-aminocaproic acid polymer (6-nylon, N1) as used in Example 3, 6,6-nylon (N3) having a melting point of 265° C. according to the DTA method in which the temperature-elevating rate was 10° C./min and an oxygen permeability of 0.69×10^{-12} cc-cm/cm²-sec-cmHg as measured at a temperature of 37° C. and a relative humidity of 0%, and an 80/20 (weight ratio) mixture (N13) of 6-nylon and 6,6-nylon having a melting point of 228° C. as measured according to the above DTA method and an oxygen permeability of 2.2×10^{-12} cc-cm/cm²-sec-cmHg were used as the intermediate layer-constituting resin. A 4-methyl-pentene-1 polymer (manufactured and sold under tradename "TPX" by ICI) having a density of 0.835 g/cc, a melting point of 228° C. as measured according to the above DTA method and a melt index of about 7.0 as measured under conditions of a load of 5 Kg and a temperature of 265° C. was used as the resin constituting innermost and outermost layers. Adhesive polypropylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a density of 0.90 g/cc, a melting point of 153° C. as measured according to the above DTA method and a melt index of 2.4 as measured according to the method of JIS K-6760 was used as the resin constituting an adhesive layer interposed between the innermost or outermost layer and the intermediate layer. In the same manner as described in Example 2, the sheet-forming operation was carried out while adjusting the rotation number of the screw so that the innermost or outermost layer/adhesive layer/intermediate layer thickness ratio was as close to as 100:5:10 as possible.

The so prepared three kinds of sheets were sufficiently heated in a hot air-circulated oven installed with an infrared heater maintained precisely at a molding temperature indicated in Table 6, and they were formed into cylindrical cups having a diameter of 85 mm, a height of 50 mm, an inner capacity of 300 cc and a unit weight of 9 to 10 g per cup according to the known plug assist air-pressure forming method.

For comparison, the foregoing three kinds of sheets were heated at 250° C. in the above-mentioned oven just after formation of the sheets and they were formed into cylindrical cups having the same configurations as described above according to the plug assist air-pressure forming method.

With respect to each of the so obtained 6 kinds of cups, the peel strength, the thickness unevenness in both the vertical and circumferential directions of the cup and the standard deviations δL and δH were determined to obtain results shown in Table 6.

As will be apparent from the results shown in Table 6, as compared with the normal heat forming method conducted at 265° C., in the solid phase pressure forming method conducted at 226° C., resin combinations satisfying the requirements of the present invention give generally better results.

In the above-mentioned DTA method, the melting-initiating temperature (the temperature at which melting endotherm takes place in the DTA thermogram) of 6-nylon (N1) was 209° C. and the melting-ending temperature (the temperature at which melting endotherm is completed in the DTA thermogram) was 229° C. The melting-initiating temperature of the blend (N13) of 6-nylon and 6,6-nylon was 203° C. and the melting-ending temperature of the nylon blend was 232° C. The melting-initiating and melting-ending temperatures of 6,6-nylon were 246° C. and 268° C., respectively. Accordingly, when the forming was carried out at 226° C., 6-nylon (N1) and nylon blend (N13) were in the semi-molten state and 6,6-nylon was maintained at the forming step at a temperature much lower than the melting-initiating temperature (246° C.).

Table 6

Intermediate Layer-Constituting Material	Forming Temperature (°C.)	Peel Strength (g/1 cm width)		Thickness Unevenness	
		Intermediate layer-adhesive layer	Adhesive layer-innermost or outermost layer	δL	δH
N1	226	935	410	0.15	0.09
N3	226	15	20	0.20	0.12
N13	226	930	420	0.13	0.10
N1	268	930	420	0.42	0.12
N3	268	1030	380	0.50	0.11

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Table 6-continued

Intermediate Layer-Constituting Material	Forming Temperature (°C.)	Peel Strength (g/1 cm width)		Thickness Unevenness	
		Intermediate layer-adhesive layer	Adhesive layer-innermost or outermost layer	δL	δH
N13	268	920	480	0.43	0.15

EXAMPLE 5

Four kinds of sheets prepared in Example 2 were

peel strength between the intermediate and adhesive layers and the haze, are lowered to levels before rolling.

Table 7

Sheet	Intermediate Layer	Tray-Forming Temperature (°C.)	Peel Strength* (g/1 cm width)		Orientation Coeffi-** cients (innermost and outermost layers)			Haze (Hz) (%)
			intermediate layer-adhesive layer	adhesive layer-innermost or outermost layer	l	m	n	
Unrolled Sheet	EV1		285	not peeled	0.02	0.01	0.97	21
	EV2		320	"	0.01	0.03	0.96	20
	EV3		430	"	0.02	0.01	0.97	21
	EV4		250	"	0.03	0.02	0.95	19
Cold-Rolled Sheet	EV1		420	"	0.20	0.08	0.72	12
	EV2		525	"	0.21	0.07	0.72	13
	EV3		930	"	0.21	0.06	0.73	11
	EV4		390	"	0.20	0.05	0.75	15
	EV1	155	415	"	0.38	0.18	0.44	8
	EV2	155	520	"	0.45	0.15	0.40	7
	EV3	155	<10***	"	0.35	0.18	0.47	7
	EV4	155	395	"	0.37	0.17	0.46	13
	EV1	210	283	"	0.03	0.02	0.95	18
	EV2	210	310	"	0.03	0.02	0.95	19
	EV3	210	450	"	0.02	0.01	0.95	21
	EV4	210	310	"	0.03	0.01	0.96	20

Notes
*: average value (sample number = 15)
**: l direction designates the rolling direction of the starting sheet, which corresponds to the direction of the long axis of the rectangular shape of the tray.
***: delamination was caused between the intermediate and adhesive layers of the tray.

subjected to cold rolling at a rolling speed of about 5 m/min at room temperature by using a roll. The sheet thickness after the cold rolling was about 0.40 mm. The cold-rolled sheets were heated at a tray-forming temperature precisely controlled to a level indicated in Table 7 and then formed in rectangular trays having a length of 140 mm, a width of 100 mm and a depth of 25 mm under a forming pressure of 5 to 9 Kg/cm² according to the known plug assist air-pressure forming method.

For comparison, the foregoing 4 kinds of cold-rolled sheets were sufficiently heated at about 210° C. and formed in rectangular trays having the same dimensions as described above according to the plug assist air-pressure forming method.

With respect to each of the foregoing 4 kinds of sheets before cold rolling, the foregoing 4 kinds of cold-rolled sheets and the foregoing 8 kinds of formed trays, in the same manner as described in Example 1, the peel strength and orientation coefficients (l, m and n) were determined. With respect to each of the foregoing 8 kinds of trays, the haze (Hz) was determined according to the method of JIS K-6714. Results are shown in Table 7.

As will be apparent from the results shown in Table 7, even when rolled sheets are formed into trays, if the requirements of the present invention are satisfied, the properties of trays can be remarkably improved. It will also be understood that even if properties are improved by rolling, when normal heat forming is conducted on rolled sheets, the improved properties, for example, the

EXAMPLE 6

Symmetric 7-layer sheets composed of four resins were prepared from the same resin combination as that used in Example 1 for formation of innermost, outermost, intermediate and adhesive layers, and additionally, sheet scraps formed at the forming step in this Example and scraps formed by crushing defective cups formed in this Example by a crusher were used as the resin material for formation of layers interposed between the innermost layer and adhesive layer and between the outermost layer and adhesive layer. From these resin materials, symmetric 7-layer sheets having a thickness of about 0.8 mm and a width of 450 mm were molded by using the same extruder for formation of innermost and outermost layers, the same extruder for formation of adhesive layers, the same extruder for formation of intermediate layers and the same sheet-winding machine as used in Example 2, and additionally, an extruder for formation of intervening layers, which was installed with a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, and a sheet extrusion molding machine comprising a multi-channel adaptor and a T-die having a lip width of 0.8 mm and a lip length of 500 mm were used for the sheet-forming operation. The screw rotation numbers of the four extruders were adjusted so that in the molded sheets, the thickness ratio of innermost or outer-

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most layer/intervening layer/adhesive layer/intermediate layer was as close to 100:20:5:10 as possible.

The so obtained 4 kinds of sheets were sufficiently heated at 155° C. and then formed into cylindrical cups having the same configurations and unit weight as those of the cups prepared in Example 2 according to the known plug assist air-pressure forming method. For comparison, these sheets were formed into cylindrical cups having the same configurations and unit weight as above according to the sheet blow molding method as in Example 2.

Cups prepared by plug assist air-pressure forming (solid phase forming) by using EV1 as the intermediate layer-constituting resin were designated as "SR1" and cups prepared by sheet blow molding of molten sheets containing EV1 as the intermediate layer-constituting resin were designated as "SBB1". Similarly, cups formed by plug assist air-pressure forming by using EV2, EV3 and EV4 and cups formed by sheet blow molding by using EV2, and EV3 and EV4 were designated as "SPR2", "SPR3", "SPR4", "SBB2", "SBB3" and "SBB4", respectively.

With respect to each of these 8 kinds of cups, the oxygen transmission rate (QO_2), haze (Hz), orientation coefficients (l, m and n), vibration resistance (N, ADN) and thickness unevenness (δL and δH) in the intermediate layer were determined in the same manner as described in Example 2 to obtain results shown in Table 8.

From the results shown in Table 8, it will readily be understood that the transparency of cups obtained in this Example is inferior to that of the cups obtained in Example 2 because of the presence of intervening layers of scraps, but a similar tendency is observed in this Example with respect to other items and cups having excellent properties can be obtained if the requirements of this invention are satisfied.

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0.91 g/cc as measured according to the method of ASTM D-1505 (data of density given hereinafter are those determined by the same method) and a melting point of 165° C. as measured according to the DTA method was used as the resin constituting the outer and inner layers. A modified low density polyethylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a melt index of 2.0 g/10 min, a density of 0.92 g/cc, a melting point of 113° C. as measured according to the DTA method and a carbonyl group concentration of 180 millimoles per 100 g of the polymer was used as the adhesive layer-constituting resin. An ethylene-vinyl alcohol copolymer having an ethylene content of 35 mole %, a vinyl alcohol content of 64.5 mole %, a residual vinyl acetate content of 0.5 mole %, a melting point of 164° C. as measured according to the DTA method (temperature-elevating rate = 10° C./min) and an oxygen permeability of 0.16×10^{-12} cc-cm/cm²·sec·cmHg as measured at a temperature of 37° C. and a relative humidity of 0% was used as the oxygen-barrier intermediate layer. Parisons of this multi-layer structure were designated as "parisons A".

Bottomless laminate pipes (laminate parisons) having the same symmetric 5-layer structure as described above were prepared by using the same co-extrusion equipment as described above. The same resins as described above were used for formation of outer, inner and intermediate layers, but as the adhesive layer-constituting resin, there was employed a modified polypropylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a melt index of 2.0 g/10 min, a density of 0.91 g/cc, a melting point of 160° C. as measured according to the DAT method and a carbonyl group concentration of 167 millimoles per 100 g of the polymer. The pipes (pari-

Table 8

Symbol of Cup	QO_2, cc/m²·day·atm	Hz (%) (cup)	Orientation Coefficients (innermost and outermost layers)			Vibration Test Results		Thickness Unevenness in Intermediate Layer	
			γ	m	n	N	ADN	δL	δH
SPR1	1.7	12	0.32	0.10	0.58	0	0	0.19	0.09
SPR2	0.6	9	0.39	0.10	0.51	0	0	0.14	0.09
SPR3	0.6	7	0.31	0.14	0.55	0	2	0.20	0.11
SPR4	20.2	18	0.32	0.15	0.53	0	1	0.53	0.29
SBR1	3.8	26	0.03	0.01	0.96	0	1	0.21	0.13
SBR2	3.2	24	0.04	0.01	0.95	1	2	0.19	0.14
SBR3	2.8	25	0.02	0.02	0.96	1	1	0.20	0.13
SBR4	31.0	27	0.04	0.01	0.95	1	2	0.21	0.12

EXAMPLE 7

Bottom-less laminate pipes (laminate parisons) having a symmetric 5-layer structure of outer layer/adhesive layer/oxygen-barrier (intermediate layer)/adhesive layer/inner layer were prepared by using an extruder for formation of intermediate layers having a diameter of 40 mm, an effective length of 880 mm and one melt channel passage, an extruder for formation of adhesive layers having a diameter of 40 mm, an effective length of 880 mm and 2 melt channel passages, an extruder for formation of outer and inner layers having a diameter of 65 mm, an effective length of 1430 mm and 2 melt channel passages and a 5-ply die for co-extrusion.

An isotactic homopolypropylene having a melt index of 0.5 g/10 min as measured according to the method of ASTM D-1238 (data of melt index given hereinafter are those as determined by the same method), a density of

sons) were designated as "pipes B".

In each of the pipes A and B, the total thickness was about 10 mm, the inner diameter was 30 mm and the length was 30 mm, and the thickness ratio of outer layer/adhesive layer/intermediate layer/adhesive layer/inner layer was 1:1/20:1/50:1/20:1.

The pipes (parisons) A and B were heated for 35 minutes in an atmosphere maintained at 158±0.5° C. Both the ends of each pipe were clamped by clamps, and the pipe was drawn in the longitudinal direction. Then, the pipe was gripped by a mold for blow molding and air was introduced under pressure from one end to inflate the parison in the lateral direction. Thus, biaxially drawn blow bottles having a symmetric 5-layer structure were prepared. In the so obtained bottles, the inner diameter was 100 mm, the height is 150 mm, the average thickness of the bottle wall was 0.6 mm, the inner capacity was about 1180 cc and the unit volume

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was 0.31 dl/g. The bottles had a cylindrical shape, and it was confirmed that in each bottle, the multi-layer structure was the same as the above-mentioned structure of the parison. Bottles prepared from parisons A and from parisons B were designated as "bottles AB" and "bottles BB", respectively.

With respect to each of the so obtained bottles, the oxygen permeability (QO_2) was determined according to the method described in Japanese Pat. Publication No. 11263/77, and the haze (Hz) was determined according to the method of JIS K-6714. Further, the bottles were subjected to the falling test described below to determine the impact resistance (SB) and delamination resistance (LB). The falling test was conducted in the following manner.

Twenty bottles were optionally chosen from each of groups AB and BB of bottles, and 1150 cc of an aqueous solution of table salt was filled in each sample bottle. The filled bottles were allowed to stand over 3 days and nights in an atmosphere maintained at −1° C. and they were let to fall on a concrete floor from a height of 100 cm in an atmosphere maintained at 20° C. so that bottoms of the bottles hit on the concrete floor, and the falling strength (impact resistance represented by $S_B = 100 \times [20 - S_1]/20$ in which S_1 represents a number of bottles broken at the first falling test) was determined. Further, with respect to N of bottles which were not broken in the above falling test, occurrence of delamination in the bottom portion, barrel portion, shoulder portion and mouth portion was visually checked by a panel of 5 men, and the delamination resistance ($L_B = 100 \times [N - L_1]/N$ in which L_1 represents a number of bottles in which it was judged that delamination took place, among N of bottles which were not broken at the first falling test) was determined. Obtained results are shown in Table 9.

As will be apparent from the results shown in Table 9, there is no substantial difference between bottles AB and BB with respect to the oxygen permeability (QO_2) and haze (Hz), but bottles AB are apparently excellent over bottles BB with respect to the measured values of impact strength (S_B) and delamination resistance (L_B). Thus, it is seen that blow bottles AB formed by heating formed pipes to melt the adhesive layer-constituting resin and then biaxially drawing the pipes are much excellent over blow bottles BB formed by conducting biaxial drawing without melting the adhesive resin layer-constituting resin with respect to the impact resistance and delamination resistance.

When pipes B were heated for 20 minutes in an atmosphere maintained at 198°±1° C., the pipes were molten and they could not retain their shapes. Accordingly, in this case biaxial drawing was impossible.

EXAMPLE 9

	Bottle AB	Bottle BB
Oxygen Permeability (QO_2, cc/m² . day . atm)	10.0	10.4
Haze (Hz, %)	8.4	8.5
Impact Resistance (S_B, %)	90	60
Delamination Resistance (L_B, %)	72.2	0

EXAMPLE 8

Sheets having a symmetric 5-layer structure of outermost layer/adhesive layer-oxygen-barrier layer (intermediate layer)/adhesive layer/innermost layer were

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prepared by using an extruder for formation of outermost and innermost layers, which was installed with a full-flighted screw having a diameter of 65 mm and an effective length of 1430 mm and had 2 divided flow passages (melt channels), an extruder for formation of adhesive layers, which was installed with a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm and had 2 divided melt channels, an extruder for formation of intermediate layers, which was installed with a full-flighted screw having a diameter of 40 mm and an effective length of 880 mm, a 5-ply T-die having a lip width of 0.6 mm and a lip length of 500 mm and a sheet-forming machine.

The same ethylene-vinyl alcohol copolymers EV1 and EV2 as used in Example 1 and an ethylene-vinyl alcohol copolymer (EV-5) having an ethylene content of 63 mole %, a vinyl alcohol content of 37 mole %, a melting point of 128° C. as the DTA method described in Example 1 and an oxygen permeability of 4.4×10^{-12} cc-cm/cm²-sec-cmHg as measured under the conditions described in Example 1 were used as the intermediate layer-constituting resin. Low-pressure polyethylene (HDPE) having a density of 0.955 g/cc, a melting point of 131° C. as measured according to the DTA method and a melt index of 0.3 g/10 min as measured according to the method of JIS K-6760 and medium low-pressure polyethylene (MDPE) having a density of 0.935 g/cc, a melting point of 122° C. as measured according to the DTA method and a melt index of 1.0 g/10 min as measured according to the above method were used as the resin constituting the innermost and outermost layers. A modified low density polyethylene (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a density of 0.92 g/cc, a melting point of 114° C. as measured according to the DTA method, a melt index of 0.3 g/10 min as measured according to the above method and a carbonyl group concentration of 48 millimoles per 100 g of the polymer was used as the adhesive layer-constituting resin.

In the so formed sheets, the thickness was about 0.8 mm and the width was about 450 mm. At the sheet-forming step, the rotation rates of the screws of the three extruders were adjusted so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:5:10 as possible.

The so prepared 6 kinds of sheets were cold-rolled at room temperature at a rolling speed of about 5 m/min by using a pair of rolls having a diameter of 10 mm and a width of 500 mm. The cold-rolled sheets had a thickness of about 0.35 mm. Then, the rolled sheets were sufficiently heated in a hot air-circulated oven maintained precisely at a forming temperature indicated in Table 10. Then, the sheets were formed under a pressure of 5 to 9 Kg/cm² into rectangular trays having a length of 140 mm, a width of 100 mm and a depth of 25 mm according to the known plug assist air-pressure forming method.

For comparison, the foregoing 6 kinds of cold-rolled sheets were heated sufficiently at 190° or 200° C. and then, they were formed into rectangular trays having the same configurations as described above according to the plug assist air-pressure forming method.

With respect to each of 6 kinds of sheets before cold rolling, 6 kinds of cold-rolled sheets and 12 kinds of so prepared trays, specimens having a width of 10 mm and a length of 50 mm were cut off, the interlaminar peel strength (intermediate layer-adhesive layer and adhe-

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sive layer-innermost or outermost layer) was measured at a peeling speed of 100 mm/min in an atmosphere

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quirements of the present invention are collectively excellent.

Table 10

	Layer-Constituting Resins			Peel Strength [g/cm width]	
Sheet	Interme-diate Layer	Innermost and Outermost Layers	Tray-Forming Temperature (°C)	Intermediate layer-adhesive layer	Adhesive layer innermost or outermost layer
Unrolled Sheet	EV1	HDPE		191	not peeled
	"	MDPE		220	"
	EV2	HDPE		119	"
	"	MDPE		184	"
	EV5	HDPE		189	"
	"	MDPE		168	"
Cold-Rolled Sheet	EV1	HDPE		1020	"
	"	MDPE		1130	"
	EV2	HDPE		1060	"
	"	MDPE		1100	"
	EV5	HDPE		1090	"
	"	HDPE		980	"
Cold-Rolled Sheet	EV1	HDPE	129	1005	"
	"	MDPE	118	150	"
	EV2	HDPE	129	655	"
	"	MDPE	118	135	"
	EV5	HDPE	129	1030	"
	"	MDPE	118	950	"
	EV1	HDPE	195	160	"
	"	MDPE	195	173	"
	EV2	HDPE	200	110	"
	"	MDPE	200	170	"
	EV5	HDPE	195	185	"
	"	MDPE	195	153	"

	Layer-Constituting Resins		Orientation Coefficients** (innermost and outermost layers)			Haze (Hz)
Sheet	Interme-diate layer	Innermost and Outermost layers	l	m	n	(%)
Unrolled Sheet	EV1	HDPE	0.02	0.01	0.97	—
	"	MDPE	0.01	0.01	0.98	—
	EV2	HDPE	0.02	0.01	0.97	—
	"	MDPE	0.01	0.02	0.97	—
	EV5	HDPE	0.01	0.01	0.98	—
	"	MDPE	0.03	0.01	0.96	—
Cold-Rolled Sheet	EV1	HDPE	0.19	0.08	0.73	—
	"	MDPE	0.17	0.09	0.74	—
	EV2	HDPE	0.21	0.06	0.73	—
	"	MDPE	0.22	0.09	0.69	—
	EV5	HDPE	0.18	0.10	0.72	—
	"	MDPE	0.19	0.07	0.74	—
Cold-Rolled Sheet	EV1	HDPE	0.19	0.11	0.70	42
	"	MDPE	0.18	0.10	0.72	30
	EV2	HDPE	0.22	0.11	0.67	—
	"	MDPE	0.23	0.09	0.68	—
	EV5	HDPE	0.19	0.10	0.71	—
	"	MDPE	0.20	0.08	0.72	—
	EV1	HDPE	0.03	0.02	0.95	78
	"	MDPE	0.02	0.04	0.94	62
	EV2	HDPE	0.04	0.03	0.93	82
	"	MDPE	0.02	0.04	0.95	51
	EV5	HDPE	0.03	0.02	0.95	79
	"	MDPE	0.04	0.03	0.93	53

Notes
*: average value (sample number = 10)
**: l direction of the tray corresponds to the rolling direction of the starting sheet and to the direction of the long axis of the rectangular shape of the tray.

maintained at a temperature of 20° C. and a relative humidity of 60%, and the orientation coefficients (l, m and n) of the intermediate layer were determined according to the fluorescent method described hereinbefore. Further, with respect to 12 kinds of the resulting trays, the haze (Hz) was determined according to the method of JIS K-6714. Test results are shown in Table 10.

As will be apparent from the results shown in Table 10, trays prepared from resin combinations HDPE-EV1, HDPE-EV2 and MDPE-EV5 meeting the re-

EXAMPLE 9

Symmetric 5-layer sheets having a thickness of 0.8 mm and a width of 450 mm were formed by using the extruding and sheet-forming equipment system described in Example 8. The rotation numbers of the screws were adjusted as in Example 8 so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:5:10 as possible.

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The same ethylene-vinyl alcohol copolymers EV1 and EV2 as used in Example 1 were used as the intermediate layer-constituting resin. Polybutene-1 having a density of 0.915 g/cc, a melting point of 129° C. as

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cluding EV1 as the intermediate layer constituting resin and meeting the requirements of the present invention are used and the forming temperature is adjusted to 125° C.

Table 11

Intermediate Layer-Constituting Resin	Forming Temperature (°C.)	Oxygen Permeability (QO₂) (cc/m² . day . atm)	Falling Strength (Sɪ) [%]	Delamination Resistance (Lɪ) [%]
EV1	125	1.2	100	100
EV2	125	0.4	90	90.0
EV1	200	2.1	80	87.5
EV2	200	0.3	70	71.4

measured according to the DTA method and a melt flow index of 0.1 g/10 min as measured according to the method of ASTM D1238 (condition E) was used as the resin constituting the innermost and outermost layers.

A modified ethylene-vinyl acetate copolymer (manufactured and sold under tradename "MODIC" by Mitsubishi Petrochemical) having a density of 0.94 g/cc, a melting point of 93° C. as measured according to the DTA method, a melt index of 2.0 g/10 min as measured according to the method of JIS K-6760 and a carbonyl group concentration of 240 millimoles per 100 g of the polymer was used as the resin constituting the adhesive layer between the intermediate layer and the innermost or outermost layer.

Two kinds of the so prepared sheets were sufficiently heated in a hot air-circulated oven maintained precisely at a forming temperature indicated in Table 11 and installed with an infrared heater, and then, they were formed into cylindrical cups having a diameter of 85 mm, a height of 50 mm, an inner capacity of 300 cc and a unit weight of 9 to 10 g per cup according to the known plug assist air-pressure forming method.

For comparison, the foregoing 2 kinds of sheets were sufficiently heated at 190° to 200° C. in the above-mentioned oven and they were formed into cylindrical cups having the same dimensions as described above according to plug assist air-pressure forming method.

With respect to each of the so prepared 4 kinds of cups, the oxygen permeability (QO₂) was determined according to the method described in Example 7. Ten cups were chosen from each of the foregoing 4 kinds of cups, and 340 g of an aqueous solution of table salt was filled in each cup and an aluminum lid was attached to each cup by means of a seamer. Then, the cups were allowed to stand in an atmosphere maintained at −1° C. over three days and nights, and immediately, they were let to fall on a concrete floor from a height of 3 mm in an atmosphere maintained at 20° C. so that the bottoms hit on the concrete floor. The falling strength (Sɪ) was calculated according to the method described in Example 7, and the delamination resistance (Lɪ defined in Example 7) was visually evaluated by a panel of 5 men. Obtained results are shown in Table 11.

As will be apparent from the results shown in Table 11, cups excellent in oxygen-barrier property and falling strength can be obtained when resin combinations in-

EXAMPLE 10

Symmetric 5-layer sheets having a thickness of about 0.8 mm and a width of 450 mm were formed by using the extruding and sheet-forming equipment system described in Example 8. The rotation numbers of the screws of the extruders were adjusted so that the thickness ratio of innermost or outermost layer/adhesive layer/intermediate layer was as close to 100:5:10 as possible.

The same ethylene-vinyl alcohol copolymers EV1, EV2 and EV5 as used in Example 1 were employed as the intermediate layer-constituting resin. A polycarbonate (PC) synthesized from phosgene and bisphenol-A, which had a softening point of 160° C. as measured according to the torsion rigidity measurement method, and poly(methyl methacrylate) (PMMA) having a glass transition temperature of 115° C. as measured according to the DTA method were used as the resin constituting the innermost and outermost layers. The same modified ethylene-vinyl acetate copolymer as used in Example 8 was used as the resin constituting the adhesive layer between the intermediate layer and the innermost or outermost layer.

The so prepared 6 kinds of sheets were formed into cylindrical cups having the same configurations and unit weight as those of the cups prepared in Example 9 at a forming temperature indicated in Table 12 according to the known plug assist air-pressure forming method.

With respect to each of the so formed 6 kinds of cups, the orientation coefficients (l, m and n) of the intermediate layer were determined according to the above-mentioned fluorescence method, the interlaminar peel strength between the intermediate layer and adhesive layer was measured according to the method described in Example 8, and the thickness unevenness (standard deviations δL and δH) in the vertical direction and circumferential direction of the cup was determined. Obtained results are shown in Table 12.

From the results shown in Table 12, it will readily be understood that when resin combinations meeting the requirements of the present invention are employed, cups collectively excellent in various properties can be obtained.

Table 12

Layer-Constituting Resins		Forming Temperature (°C.)	Orientation Coefficients			Thickness Uniformity in Cup		Peel Strength (g/cm) width (intermediate layer-adhesive layer)
Intermediate Layer	Innermost or outermost layer		l	m	n	δL	δH	
EV1	PC	153	0.32	0.10	0.58	0.15	0.07	490
EV3	PC	153	0.29	0.12	0.59	0.20	0.10	< 10
EV5	PC	153	0.30	0.09	0.61	0.19	0.15	235
EV1	PMMA	105	0.25	0.09	0.56	0.23	0.06	253

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Table 12-continued

Layer-Constituting Resins		Forming Tempera-ture (°C.)	Orientation Coefficients			Thickness Uniformity in Cap		Peel Strength (g/cm) width) (intermediate layer-adhesive layer)
Interme-diate Layer	Innermost or outermost layer		l	m	n	8L	8H	
EV3	PMMA	105	0.27	0.06	0.67	0.25	0.12	<10
EV5	PMMA	105	0.23	0.07	0.70	0.21	0.14	135

What we claim is:

1. A transparent multi-layer varied thickness container obtained by draw-forming a parison composed of a coextrudate of at least one oxygen barrier thermoplastic resin layer and at least one crystalline polyolefin layer, said oxygen barrier thermoplastic resin having an oxygen permeability lower than 5.5×10^{-12} cc-cm/c-m²-sec-cmHg as measured at 37° C. and being selected from the group consisting of a copolymer consisting essentially of ethylene and vinyl alcohol and a polyamide, wherein said oxygen barrier thermoplastic resin and said polyolefin are selected so that the requirement represented by the following formula:

$$|T_B - T_O| \leq 15° \text{ C.}$$

wherein T_B stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin and T_O stands for the melting or softening point (°C.) of said polyolefin, is satisfied, and wherein at least one of two-dimensional orientation coefficients (l and m) of at least one layer composed of said polyolefin in a smallest-thickness portion of the container is at least 0.05.

2. A container as set forth in claim 1 wherein the oxygen barrier thermoplastic resin is an ethylenevinyl alcohol copolymer containing vinyl alcohol units at a content satisfying the requirement represented by the following formula:

$$0.61T_O - 56.1 \leq X \leq 0.61T_O - 24.2$$

wherein T_O stands for the melting or softening point (°C.) of the polyolefin and X stands for the content (mole %) of the vinyl alcohol units in the oxygen barrier thermoplastic resin.

3. A container as set forth in claim 1 wherein the oxygen barrier thermoplastic resin and the polyolefin are selected so that the requirement represented by the following formula:

$$|T_B - T_O| \leq 10° \text{ C.}$$

wherein T_B and T_O are as defined above, is satisfied, at least one of two-dimensional orientation coefficients (l and m) of at least one layer of the polyolefin in a smallest-thickness portion of the container is at least 0.1, each resin layer has a haze (Hz) lower than 10%, and wherein the bonding strength between every two adjacent layers is at least 20 g/cm.

4. A container as set forth in claim 1 wherein the poloylefin is a crystalline polypropylene or a crystalline ethylene-propylene copolymer having an ethylene content of 1 to 20 mole %.

5. A container as set forth in claim 1 wherein the polyolefin is present on both the surfaces of the container as the outermost and innermost layers and the oxygen barrier thermoplastic resin is present as the intermediate layer of the container.

6. A transparent multi-layer varied thickness container obtained by draw-forming a parison composed of a co-extrudate of at least one layer composed of (A) an oxygen barrier thermoplastic resin having an oxygen permeability lower than 5.5×10^{-12} cc-cm/c-m²-sec-cmHg as measured at 37° C., at least one layer

comprising (B) a crystalline polyolefin and at least one layer interposed between said oxygen barrier thermoplastic resin layer and said polyolefin layer and being composed of (C) a resin having an adhesiveness to both of said resins, said oxygen barrier thermoplastic resin being selected from the group consisting of a copolymer consisting essentially of ethylene and vinyl alcohol and a polyamide, said adhesive resin being a polyolefin modified with at least one ethylenically unsaturated monomer selected from the group consisting of unsaturated carboxylic acids and anhydrides, esters and amides thereof containing carbonyl groups at a concentration of 10 to 1400 millimols per 100 g of the polymer, wherein said three resins are selected so that the requirements represented by the following formulae:

$$|T_B - T_O| \leq 15° \text{ C.}$$

and

$$90° \text{ C.} \geq T_O - T_C \geq 2° \text{ C.}$$

wherein T_B stands for the melting or softening point (°C.) of said oxygen-barrier thermoplastic resin, T_O stands for the melting or softening point (°C.) of said polyolefin and T_C stands for the melting or softening point (°C.) of said adhesive resin, at least one of two-dimensional orientation coefficients (l and m) of at least one layer composed of said polyolefin in a smallest-thickness portion of the container is at least 0.05, and wherein the layer of said adhesive resin is substantially non-oriented.

7. A container as set forth in claim 6 wherein the polyolefin (B) is a crystalline polypropylene or a crystalline ethylene-propylene copolymer having an ethylene content of 1 to 20 mole %, the layer comprising said polyolefin is present on both the surfaces of the container as the outermost and innermost layers, the oxygen barrier thermoplastic resin (A) is a copolymer consisting essentially of ethylene and vinyl alcohol and containing vinyl alcohol units at a content satisfying the requirement represented by the following formula:

$$0.61T_O - 56.1 \leq X \leq 0.61T_O - 24.2$$

wherein T_O stands for the melting or softening point (°C.) of the polyolefin (B) and X stands for the content (mole %) of the vinyl alcohol units in the oxygen barrier thermoplastic resin (A), the layer of said oxygen barrier thermoplastic resin is present as the intermediate layer of the container, the adhesive resin (C) is present as the adhesive layer interposed between the outer surface layer and the intermediate layer and as the adhesive layer interposed between the inner surface layer and the intermediate layer, and wherein the thickness ration of the respective resin layers is in the following range:

(B):(A)=from 1:1 to 500:1 and

(B):(C)=from 1:1 to 500:1.

8. A container as set forth in claim 6 which is a biaxially drawn plastic bottle.

9. A container as set forth in claim 6 which is a draw-formed plastic cup.

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United States Patent [19]

Christensen et al.

[11]   **4,405,667**

[45]   Sep. 20, 1983

[54] **RETORTABLE PACKAGING STRUCTURE**

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[58] Field of Search 428/35, 475.5, 428/475.8, 476.1, 516, 523; 206/484, 484.2, 206/548.2; 426/113, 127

[56]   References Cited

U.S. PATENT DOCUMENTS

4,275,119	6/1981	Weiner	428/35
4,276,330	6/1981	Stanley et al.	428/35
4,303,710	12/1981	Ballard et al.	428/35
4,308,084	12/1981	Ohtsuki et al.	428/35
4,355,721	10/1982	Knott et al.	428/35
4,356,221	10/1982	Anthony et al.	428/35
4,357,376	11/1982	Nattinger et al.	428/35
4,360,551	11/1982	Guarino et al.	428/35
4,364,981	12/1982	Homer et al.	428/35

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[57]   ABSTRACT

A retortable pouch is made without the use of metal foil. The improved heat sealable structure has an inner heat seal layer of linear low density polyethylene. The second, or adjacent layer is a blend of 20% to 80% linear low density polyethylene and 80% to 20% propylene ethylene copolymer. Optional third, fourth and fifth layers are propylene ethylene copolymer. A sixth layer is anhydride modified polypropylene. A seventh layer is nylon, the eighth layer is ethylene vinyl alcohol copolymer and the ninth layer is nylon. The entire multiple layer structure is firmly adhered together so that the layers mutually support each other in the unitary package.

9 Claims, 6 Drawing Figures